
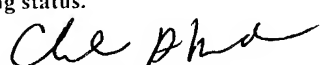


12-28-01

FORM PTO-1300 (REV. 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER 427.051	
<b>TRANSMITTAL LETTER TO THE UNITED STATES          DESIGNATED/ELECTED OFFICE (DO/EO/US)          CONCERNING A FILING UNDER 35 U.S.C. 371</b>				U.S. APPLICATION NUMBER <b>10/019167</b>	
INTERNATIONAL APPLICATION NO PCT/FR00/01753		INTERNATIONAL FILING DATE 6/23/00		PRIORITY DATE CLAIMED 6/25/99	
TITLE OF INVENTION POLYMERISATION CATALYSTS					
APPLICANT(S) FOR DO/EO/US Hanh Nguyen Ngoc, et al					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371. 3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below. 4. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)) a. <input checked="" type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4) 7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau) b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made, however, the time limit for making such amendments has NOT expired d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)) 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) 10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).  Items 11 to 20 below concern document(s) or information included: 11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98 12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 15. <input type="checkbox"/> A substitute specification. 16. <input type="checkbox"/> A change of power of attorney and/or address letter. 17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter 2 and 35 U.S.C. 1.821 - 1.825. 18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). 19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). 20. <input type="checkbox"/> Other items or information: <b>copy of PCT/IB/332          PTO-2038</b>					

U.S. APPLICATION NO. <b>10/019167</b>		INTERNATIONAL APPLICATION NO.		<b>531 Rec'd PTO/P</b> <b>20 DEC 2001</b>	
21. <input type="checkbox"/> The following fees are submitted <b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. .... \$1000.00  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$860.00  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$710.00  International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$690.00  International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00  <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				CALCULATIONS PTO USE ONLY           	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$ 1040.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	- 20 =		x \$18.00	\$	
Independent claims	- 3 =		x \$80.00	\$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27 The fees indicated above are reduced by 1/2.				\$	
<b>SUBTOTAL =</b>				\$ 1040.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
<b>TOTAL NATIONAL FEE =</b>				\$ 1040.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$ 40.00	
<b>TOTAL FEES ENCLOSED =</b>				\$ 1080.00	
				Amount to be refunded:	\$
				charged:	\$
a. <input type="checkbox"/> A check in the amount of \$ _____ to cover the above fees is enclosed  b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed  c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>02-2275</u> . A duplicate copy of this sheet is enclosed  d. <input checked="" type="checkbox"/> Fees are to be charged to a credit card. <b>WARNING:</b> Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038. <b>PTO-2038 in the amount of \$1080.00</b>					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO <b>Charles A. Muserlian</b> <b>Bierman, Muserlian and Lippes</b> <b>600 Third Avenue</b> <b>New York, NY 10016</b>			 <b>20311</b> PATENT TRADEMARK OFFICE		
			 SIGNATURE <b>Charles A. Muserlian</b> NAME <b>19,683</b> REGISTRATION NUMBER		

10/019167  
531 Rec'd PCT... 20 DEC 2001

Our ref: 427.051

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

-----x  
In re Application of: NGUYEN NGOC, :  
et al :  
Serial No. : :  
International Appln.  
PCT/FR00/01753  
Filed : Concurrently herewith : Filed: June 23, 2000  
For : POLYMERIZATION :  
CATALYSTS :  
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600 Third Avenue  
New York, N.Y. 10016

Dated : December 20, 2001

PRELIMINARY AMENDMENT

Assistant Commissioner of Patents  
Washington, D.C. 20231

S i r:

Please amend this application as follows:

IN THE SPECIFICATION:

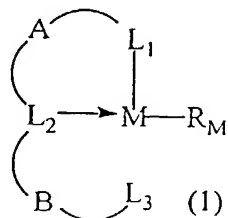
Page 1, before line 1, insert

--This application is a 371 of PCT FR00/01753, filed June  
23, 2000. --

IN THE CLAIMS

Claims 1 to 8 and 12 to 14 are amended.

--1. (Amended) A compound of the formula



wherein

M is an element of group 12 of the Periodic Table;

R<sub>M</sub> is selected from the group consisting of hydrogen, halogen, alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio, arylthio, amino, alkylamino, dialkylamino, cycloalkylamino, di(cycloalkyl)amino, alkyl(cycloalkyl)amino, arylamino, diarylamino, alkylarylamino and (cycloalkyl)arylamino;

A and B are independently selected from the group consisting of carbon chain of 2 to 4 carbon atoms, optionally substituted by at least one member of the group consisting of substituted or non-substituted alkyl, cycloalkyl, and aryl, the substituent is selected from the group consisting of halogen, alkyl, nitro and cyano;

$L_1$  and  $L_2$  are independently  $-E_{15}(R_{15})-$  in which  $E_{15}$  is an element of group 15 of the Periodic Table and  $R_{15}$  is selected from the group consisting of hydrogen, substituted or non-substituted alkyl, cycloalkyl and aryl, in which said substituent is selected from the group consisting of halogen, alkyl, nitro and cyano or  $-E_{14}RR'R''$  in which  $E_{14}$  is an element of group 14 of the Periodic Table and R, R' and R'' are independently selected from the group consisting of hydrogen, substituted or non-substituted alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio and arylthio, in which the substituents are at least one member of the group consisting of halogen, alkyl, nitro and cyano; or  $-SO_2Q$  in which Q is selected from the group consisting of halogen, alkyl, haloalkyl and aryl optionally substituted by at least one

substituent selected from the group consisting of alkyl, haloalkyl and halogen;

$L_3$  is  $-E'_{15}(R'_{15})(R''_{15})$  or  $-E_{16}(R_{16})$  in which  $E'_{15}$  is an element of group 15 of the Periodic Table and  $E_{16}$  is an element of group 16 of the Periodic Table and  $R'_{15}$ ,  $R''_{15}$  and  $R_{16}$  are, independently, selected from the group consisting of hydrogen, substituted or non-substituted alkyl, cycloalkyl and aryl, in which the substituents are at least one member of the group consisting of halogen, alkyl, nitro and cyano or  $-E'_{14}TT'T$  in which  $E'_{14}$  is an element of group 14 of the Periodic Table and  $T$ ,  $T'$  and  $T''$  are independently selected from the group consisting of hydrogen, substituted or non-substituted alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio and arylthio, in which said substituents are at least one member of the group consisting of halogen, alkyl, nitro and cyano; or  $-SO_2Q'$  in which  $Q'$  is selected from the group consisting of halogen, alkyl, haloalkyl and aryl optionally substituted by at least one member of the group consisting of alkyl, haloalkyl and halogen. --

R<sub>M</sub> is alkyl;

A and B are, independently, a carbon chain of 2 to 4 carbon atoms;

L<sub>1</sub> and L<sub>2</sub> are, independently, -E<sub>15</sub>(R<sub>15</sub>) - in which E<sub>15</sub> is nitrogen or phosphorus and R<sub>15</sub> is hydrogen or -E<sub>14</sub>RR'R" in which E<sub>14</sub> is carbon or silicon and R, R' and R" are, independently, hydrogen or alkyl;

$L_3$  is  $-E'_{15}(R'_{15})(R''_{15})$  in which  $E'_{15}$  is nitrogen or phosphorus, and  $R'_{15}$  and  $R''_{15}$  are, independently, hydrogen or  $-E'_{14}TT'T''$  in which  $E'_{14}$  is carbon or silicon atom and T, T' and T'' are independently, hydrogen or alkyl.

--4. (Amended) A compound of claim 1 wherein M is zinc. --

--5. (Amended) A compound of claim 1 wherein

$R_M$  is methyl;

A and B are, independently, a carbon chain of 2 carbon atoms;

$L_1$  and  $L_2$  are, independently,  $-E_{15}(R_{15})-$  in which  $E_{15}$  is nitrogen and  $R_{15}$  is selected from the group consisting of hydrogen, methyl, ethyl, propyl, isopropyl and  $-E_{14}RR'R''$  in which  $E_{14}$  is silicon and  $R$ ,  $R'$  and  $R''$  are, independently, selected from the group consisting of hydrogen, methyl, ethyl, propyl and isopropyl;

$L_3$  is  $-E'_{15}(R'_{15})(R''_{15})$  in which  $E'_{15}$  is nitrogen, and  $R'_{15}$  and  $R''_{15}$  are, independently, selected from the group consisting of hydrogen, methyl, ethyl, propyl, isopropyl and  $-E'_{14}TT'T''$  in which  $E'_{14}$  is silicon and  $T$ ,  $T'$  and  $T''$  are, independently, selected from the group consisting of hydrogen, methyl, ethyl, propyl, and isopropyl. --

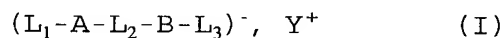
--6. (Amended) A compound of claim 1 which is

-  $[Me_3SiN(H)CH_2CH_2N(Me)CH_2CH_2NSiMe_3]ZnMe$ ; or

-  $[Me_3SiN(H)CH_2CH_2N(H)CH_2CH_2NSiMe_3]ZnMe$ . --



- 7. (Amended) A compound of claim 6 in dimer form. --
- 8. (Amended) A process for the preparation of a compound of claim 1, comprising reacting a compound of the formula



wherein  $L_1$ , A,  $L_2$ , B and  $L_3$  are defined as claim 1 and Y is hydrogen or metal or a metallic with a compound of the formula



in which M and  $R_M$  are defined as in claim 1 and Z is a parting group, to obtain a compound of claim 1.

- 12. (Amended) A process for the preparation of block or random copolymers, or polymers which comprises contacting at least one monomer, a chain initiator and/or a regulator, a polymerization catalyst and optionally a polymerization solvent, at a temperature between ambient temperature and 250°C, for a few minutes to 300 hours, wherein the chain initiator and/or the regulator and the polymerization catalyst are a compound of claim 1. --

--13. (Amended) The process of claim 12, wherein the monomer is selected from the group consisting of epoxides, and cyclic esters. --

--14. (Amended) A polymer or copolymer prepared by the process of claim 12. --

Cancel claims 9 to 11 and add the following claims.

--15. In a process for the polymerization or copolymerization of heterocycles, the improvement comprising using as the polymerization catalyst a compound of claim 1. --

--16. The process of claim 15 wherein the heterocycle is propylene oxide. --

--17. In a process for the polymerization or copolymerization of cyclic esters, the improvement comprising using as the polymerization catalyst a compound of claim 1. --

--18. The process of claim 17 wherein the cyclic ester is that of lactic acid and/or glycolic acid. --

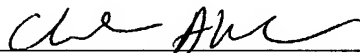
REMARKS

The amendments is submitted to insert reference to the PCT application, to remove multiple dependency from the claims and to conform the claims to the American practice.

Respectfully submitted,

Bierman, Muserlian & Lucas

By:

  
Charles A. Muserlian # 19,683  
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New York, New York 10016  
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Encl:      Marked-up copy of Amended Claims



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--This Application is a 371 of PCT FR00/01753,  
filed June 23, 2000.--

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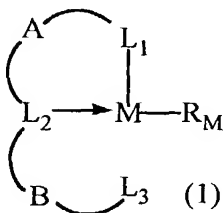
## POLYMERISATION CATALYSTS

The present invention relates to new compounds having an element of group 12 and having a tridentate ligand, a process for their preparation and their use in particular as polymerization catalysts.

5 The use of derivatives having an element of group 12 but having porphyrin type ligands (Inoue, Acc. Chem. Res., (1996) 29, 39) as catalysts for the polymerization of heterocycles is already known.

10 However, it has been shown that each type of catalyst used for the polymerizations or copolymerizations, produces different polymers or copolymers respectively (Jedlinski et al., Macromolecules, (1990) 191, 2287; Munson et al., Macromolecules, (1996) 29, 8844; Montaudou et al., Macromolecules, (1996) 29, 6461). The problem is therefore to find new catalytic systems in order to obtain new polymers or copolymers, and more particularly block copolymers. The use of catalytic systems allows control of the chain formation of monomers leading to specific copolymers having the appropriate properties. This is particularly useful for biocompatible copolymers, the biodegradation of which is  
15 influenced by this chain formation.

Therefore a subject of the invention is the products of general formula 1



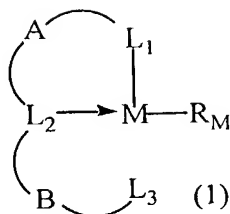
in which

- 20 M represents an element of group 12;  
R<sub>M</sub> represents the hydrogen atom, a halogen atom, or an alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio, arylthio, amino, alkylamino, dialkylamino, cycloalkylamino, di(cycloalkyl)amino, alkyl(cycloalkyl)amino, arylamino, diarylamino, alkylarylamino or  
25 (cycloalkyl)arylamino radical;

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# CLAIMS

1. <sup>AC</sup>Compounds <sup>the</sup> of general formula <sup>P</sup>



5 <sup>wherein</sup> in which

M <sup>is</sup> represents an element of group 12 <sup>of the periodic Table</sup>

R<sub>M</sub> <sup>is</sup> represents the hydrogen atom, a halogen atom, or an alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio, arylthio, amino, alkylamino, dialkylamino, cycloalkylamino, di(cycloalkyl)amino, alkyl(cycloalkyl)amino, arylamino, diarylamino, alkylaryl amino <sup>and</sup> or (cycloalkyl)aryl amino radical;

<sup>selected from the group consisting of</sup>

A and B <sup>are</sup> represent, independently, a carbon chain of 2 to 4 carbon atoms, optionally substituted by <sup>at least one member of the group consisting of</sup> one or more of the following substituted or non-substituted alkyl, cycloalkyl <sup>and</sup> or aryl radicals, <sup>the</sup> in which said substituent is a halogen atom, an alkyl, nitro <sup>and</sup> or cyano radical;

15 L<sub>1</sub> and L<sub>2</sub> <sup>are</sup> represent, independently, a group of formula -E<sub>15</sub>(R<sub>15</sub>)- in which E<sub>15</sub> is an element of group 15 <sup>and of the periodic Table</sup>

R<sub>15</sub> <sup>is</sup> represents the hydrogen atom, one of the following substituted or non-substituted alkyl, cycloalkyl <sup>and</sup> or aryl radicals, in which said substituent is a halogen atom, an alkyl, nitro <sup>and</sup> or cyano radical; a radical of formula -E<sub>14</sub>RR'R" in which E<sub>14</sub> is an element of group 14 <sup>and of the periodic Table</sup> and R, R' and R" represent, independently, the hydrogen atom or one of the following substituted (by one or more identical or different substituents) or non-substituted alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio <sup>and</sup> or arylthio radicals, in which <sup>the</sup> said substituent <sup>are at least one member of the group consisting of</sup> is a halogen atom, the alkyl, nitro <sup>and</sup> or cyano radical; or a radical of formula -SO<sub>2</sub>Q in which Q represents a

20 <sup>and</sup> halogen atom, an alkyl, haloalkyl <sup>and</sup> or aryl radical optionally substituted by

25

~~$L_3$  indifferently represents a group of formula  $-E'_{15}(R'_{15})(R''_{15})$  or  $-E_{16}(R_{16})$  in which~~

of the Periodic Table

selected from the group consisting of

non-substituted alkyl, cycloalkyl <sup>or</sup> aryl radicals, in which said substituent is

-E'<sub>14</sub>TTT" in which E'<sub>14</sub> is an element of group 14 <sup>of the periodic table</sup> and T, T' and T" <sup>are</sup> represent

cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio, <sup>and</sup>

or cyano radical: or a radical of formula  $-\text{SO}_2\text{O}'$  in which  $\text{O}'$  represents a

halogen atom, an alkyl, haloalkyl or aryl radical optionally substituted by <sup>and</sup> at least one or more substituents chosen from the alkyl, haloalkyl and halogen radicals.

2. ~~Compounds of formula 1 as defined in claim 1, characterised in that they are presented~~  
in the form of a monomer or a dimer.

3.1 <sup>A c</sup> Compounds of general formula I as defined in one of claims 1 to 2, <sup>wherein</sup> characterised in ~~that~~

~~R<sub>M</sub> represents an alkyl group;~~

A and B <sup>are</sup> represent, independently, a carbon chain of 2 to 4 carbon atoms:

L<sub>1</sub> and L<sub>2</sub> ~~represent~~<sup>are</sup>, independently, a radical of formula -E<sub>15</sub>(R<sub>15</sub>)- in which E<sub>15</sub> is a nitrogen or phosphorus atom and R<sub>15</sub> represents a hydrogen atom or a radical of formula -E<sub>14</sub>RR'R'' in which E<sub>14</sub> ~~represents~~<sup>is</sup> a carbon or silicon atom and R, R' and R'' ~~represent~~<sup>are</sup>, independently, the hydrogen atom or an alkyl radical;

L<sub>1</sub> represents a radical of formula -E'<sub>15</sub>(R'<sub>15</sub>)(R''<sub>15</sub>) in which E'<sub>15</sub> is a nitrogen or phosphorus atom, and R'<sub>15</sub> and R''<sub>15</sub> represent, independently, a hydrogen atom or a radical of formula -E'<sub>14</sub>TT'T" in which E'<sub>14</sub> represents a carbon or silicon atom and T, T' and T" represent, independently, a hydrogen atom or an alkyl radical.

4. <sup>A</sup> ~~Compounds of general formula 1 as defined in one of claims 1 to 3, characterized in~~ <sup>wherein</sup>  
that M represents a zinc atom.

5. <sup>A c</sup>Compounds of general formula 1 as defined in one of claims 1 to 4, <sup>wherein</sup> characterized in that

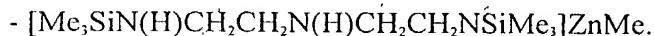
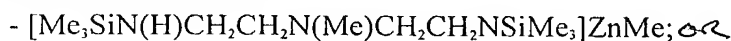
<sup>13</sup>  
R<sub>M</sub> represents a methyl radical;

A and B <sup>are</sup> represent, independently, a carbon chain of 2 carbon atoms;

5 L<sub>1</sub> and L<sub>2</sub> <sup>are</sup> represent, independently, a radical of formula -E<sub>15</sub>(R<sub>15</sub>)- in which E<sub>15</sub> is a nitrogen atom and R<sub>15</sub> <sup>15 selected from the group consisting of</sup> represents a hydrogen atom, a methyl, ethyl, propyl, isopropyl radical or a radical of formula -E<sub>14</sub>RR'R" in which E<sub>14</sub> <sup>15</sup> represents a silicon atom and R, R' and R" <sup>are</sup> represent, independently, the hydrogen atom or a methyl, ethyl, propyl or isopropyl radical;

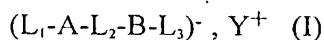
<sup>selected from the group consisting of</sup>  
L<sub>1</sub> represents a radical of formula -E'<sub>15</sub>(R'<sub>15</sub>)(R''<sub>15</sub>) in which E'<sub>15</sub> is a nitrogen atom, and R'<sub>15</sub> and R''<sub>15</sub> <sup>are</sup> represent, independently, a hydrogen atom, a methyl, ethyl, propyl, isopropyl radical or a radical of formula -E'<sub>14</sub>TT'T" in which E'<sub>14</sub> <sup>15</sup> represents a silicon atom and T, T' and T" <sup>are</sup> represent, independently, the hydrogen atom or a methyl, ethyl, propyl or isopropyl radical.

6. <sup>A c</sup>Compounds of general formula 1 as defined in one of claims 1 to 4 <sup>which is</sup> and corresponding to the following formulae:



7. <sup>A c</sup>Compounds of formula 1 as defined in claim 6, characterized in that they are presented in dimer form.

20 8. <sup>A</sup>Process for the preparation of the products of general formula 1 as defined in claim 1, characterized in that a product of formula 1 <sup>a compound of</sup> reacting a compound of the formula



<sup>wherein</sup> in which L<sub>1</sub>, A, L<sub>2</sub>, B and L<sub>3</sub> <sup>are defined as</sup> have the meanings indicated in claim 1 and Y <sup>15</sup> represents the hydrogen atom, a metal or a metallic group, is reacted with a product of formula 1 <sup>the</sup>

25  $MR_MZ \quad (II)$

in which M and R<sub>M</sub> <sup>are defined as</sup> have the meanings indicated in claim 1 and Z <sup>is</sup> represents a parting group, in order to obtain a product of formula 1.

9. Use of the products of formula 1 as defined in any one of claims 1 to 7, as polymerization or copolymerization catalyst.

30 10. Use according to claim 9 for the polymerization or copolymerization of heterocycles, in particular epoxides such as propylene oxide.

11. Use according to claim 9, for the polymerization or copolymerization of cyclic esters, in particular the polymer cyclic esters of lactic and/or glycolic acid.

12. <sup>App</sup> Process for the preparation of block or random copolymers, or polymers which ~~consist~~  
of bringing <sup>comparing</sup> into contact <sup>in at least</sup> with one or more monomers, a chain initiator and/or a regulator, a  
polymerization catalyst and optionally a polymerization solvent, at a temperature  
comprised between ambient temperature and 250° C, for a duration comprised between a  
5 few minutes <sup>to</sup> and 300 hours, said process <sup>wherein</sup> characterized in that the chain initiator and/or the  
regulator and the polymerization catalyst are <sup>are a</sup> represented by the same compound which is  
chosen from the compounds <sup>of claim 1</sup> according to claims 1 to 7.
13. <sup>The</sup> Process according to claim 12, <sup>wherein</sup> characterized in that the monomer is <sup>selected</sup> chosen from the <sup>group consisting of</sup>  
epoxides, and in particular propylene oxide, or the cyclic esters, and in particular the  
10 ~~polymer cyclic esters of lactic and/or glycolic acid.~~
14. <sup>App</sup> Polymers or copolymers <sup>prepared by the</sup> which can be obtained by carrying out a process according to  
one of claims 12 or 13. <sup>of</sup>



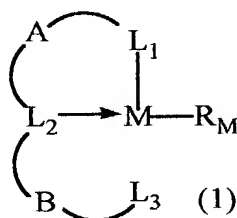
# POLYMERISATION CATALYSTS

The present invention relates to new compounds having an element of group 12 and having a tridentate ligand, a process for their preparation and their use in particular as polymerization catalysts.

5 The use of derivatives having an element of group 12 but having porphyrin type ligands (Inoue, Acc. Chem. Res., (1996) 29, 39) as catalysts for the polymerization of heterocycles is already known.

10 However, it has been shown that each type of catalyst used for the polymerizations or copolymerizations, produces different polymers or copolymers respectively (Jedlinski et al., Macromolecules, (1990) 191, 2287; Munson et al., Macromolecules, (1996) 29, 8844; Montaudou et al., Macromolecules, (1996) 29, 6461). The problem is therefore to find new catalytic systems in order to obtain new polymers or copolymers, and more particularly block copolymers. The use of catalytic systems allows control of the chain formation of monomers leading to specific copolymers having the appropriate properties. This is particularly useful for biocompatible copolymers, the biodegradation of which is  
15 influenced by this chain formation.

Therefore a subject of the invention is the products of general formula 1



in which

- 20 M represents an element of group 12;  
R<sub>M</sub> represents the hydrogen atom, a halogen atom, or an alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio, arylthio, amino, alkylamino, dialkylamino, cycloalkylamino, di(cycloalkyl)amino, alkyl(cycloalkyl)amino, arylamino, diarylamino, alkylarylamino or  
25 (cycloalkyl)arylamino radical;

- A and B represent, independently, a carbon chain of 2 to 4 carbon atoms, optionally substituted by one or more of the following substituted (by one or more identical or different substituents) or non-substituted alkyl, cycloalkyl or aryl radicals, in which said substituent is a halogen atom, the alkyl, nitro or cyano radical;
- 5 L<sub>1</sub> and L<sub>2</sub> represent, independently, a group of formula -E<sub>15</sub>(R<sub>15</sub>) - in which E<sub>15</sub> is an element of group 15 and R<sub>15</sub> represents the hydrogen atom; one of the following substituted (by one or more identical or different substituents) or non-substituted alkyl, cycloalkyl or aryl radicals, in which said substituent is a halogen atom, the alkyl, nitro or cyano radical; a radical of formula -E<sub>14</sub>RR'R" in which E<sub>14</sub> is an element of group 14 and R, R' and R" represent, independently, the hydrogen atom or one of the following substituted (by one or more identical or different substituents) or non-substituted alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio or arylthio radicals, in which said substituent is a halogen atom, the alkyl, nitro or cyano radical; or a radical of formula -SO<sub>2</sub>Q in which Q represents a halogen atom, an alkyl, haloalkyl or aryl radical optionally substituted by one or more substituents chosen from the alkyl, haloalkyl and halogen radicals.
- 10 15 20 L<sub>3</sub> indifferently represents a group of formula -E'<sub>15</sub>(R'<sub>15</sub>)(R"<sub>15</sub>) or -E<sub>16</sub>(R<sub>16</sub>) in which E'<sub>15</sub> is an element of group 15 and E<sub>16</sub> is an element of group 16 and R'<sub>15</sub>, R"<sub>15</sub> and R<sub>16</sub> represent, independently, the hydrogen atom; one of the following substituted (by one or more identical or different substituents) or non-substituted alkyl, cycloalkyl or aryl radicals, in which said substituent is a halogen atom, the alkyl, nitro or cyano radical; a radical of formula -E'<sub>14</sub>TT'T" in which E'<sub>14</sub> is an element of group 14 and T, T' and T" represent, independently, the hydrogen atom or one of the following substituted (by one or more identical or different substituents) or non-substituted alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio or arylthio radicals, in which said substituent is a halogen atom, the alkyl, nitro or cyano radical; or a radical of formula -SO<sub>2</sub>Q' in which Q' represents a halogen atom, an alkyl, haloalkyl or aryl radical optionally substituted by one or more substituents chosen from the alkyl, haloalkyl and halogen radicals.
- 25 30 35

In the definitions indicated above, the expression halogen represents a fluorine, chlorine, bromine or iodine atom, preferably chlorine. The expression alkyl preferably represents a

linear or branched alkyl radical having 1 to 6 carbon atoms and in particular an alkyl radical having 1 to 4 carbon atoms such as the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl and tert-butyl radicals.

5 The term haloalkyl preferably designates radicals in which the alkyl radical is as defined above and is substituted by one or more halogen atoms as defined above such as, for example, bromoethyl, trifluoromethyl, trifluoroethyl or also pentafluoroethyl. The alkoxy radicals can correspond to radicals in which the alkyl radical is as defined above. The methoxy, ethoxy, isopropoxy or tert-butoxy radicals are preferred. The alkylthio radicals preferably represent radicals in which the alkyl radical is as defined above such as, 10 for example, methylthio or ethylthio. The alkylamino and dialkylamino radicals preferably represent the radicals in which the alkyl radical is as defined above such as, for example, methylamino or dimethylamino.

The cycloalkyl radicals are chosen from saturated or unsaturated monocyclic cycloalkyls. The saturated monocyclic cycloalkyl radicals can be chosen from the radicals having 3 to 7 15 carbon atoms such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl or cycloheptyl radicals. The unsaturated cycloalkyl radicals can be chosen from cyclobutene, cyclopentene, cyclohexene, cyclopentadiene and cyclohexadiene radicals. The cycloalkoxy radicals can correspond to radicals in which the cycloalkyl radical is as defined above. The cyclopropyloxy, cyclopentyloxy or cyclohexyloxy radicals are preferred. The 20 cycloalkylthio radicals can correspond to radicals in which the cycloalkyl radical is as defined above such as for example cyclohexylthio. The cycloalkylamino and di(cycloalkyl)amino radicals can correspond to radicals in which the cycloalkyl radical is as defined above such as for example cyclohexylamino and di(cyclohexyl)amino.

The aryl radicals can be of mono or polycyclic type. The monocyclic aryl radicals can be 25 chosen from the phenyl radicals optionally substituted by one or more alkyl radicals, such as tolyl, xylyl, mesityl and cumenyl. The polycyclic aryl radicals can be chosen from the naphthyl, anthryl and phenanthryl radicals. The aryloxy radicals can correspond to radicals in which the aryl radical is as defined above. The phenoxy, 2,4,6-tritertibutylphenoxy, tolyloxy or mesityloxy radicals are preferred. The arylthio radicals preferably designate the 30 radicals in which the aryl radical is as defined above such as for example in phenylthio radicals. The arylamino and diarylamino radicals preferably designate radicals in which the aryl radical is as defined above such as, for example, phenylamino or diphenylamino radicals.

35 The alkyl (cycloalkyl)amino radicals can correspond to radicals in which the alkyl and cycloalkyl radicals are as defined above such as, for example methyl(cyclohexyl)amino. The alkyl arylamino radicals preferably designate radicals in which the alkyl and aryl

radicals are as defined above such as, for example methylphenylamino. The (cycloalkyl)arylamino radicals can correspond to the radicals in which the cycloalkyl and aryl radicals are as defined above such as, for example (cyclohexyl)phenylamino.

The compounds of formula 1 can be presented in the form of a monomer or of a dimer and more particularly the compounds of formula 1 in which M represents a zinc atom generally presented in dimer form.

A more particular subject of the invention is the products of general formula 1 as defined above, characterized in that

$R_M$  represents an alkyl radical;

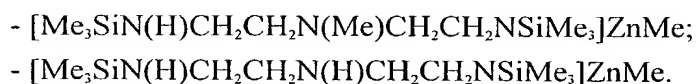
A and B represent, independently, a carbon chain with 2 to 4 carbon atoms;

$L_1$  and  $L_2$  represent, independently, a radical of formula  $-E_{15}(R_{15})-$  in which  $E_{15}$  is a nitrogen or phosphorus atom and  $R_{15}$  represents a hydrogen atom or a radical of formula  $-E_{14}RR'R''$  in which  $E_{14}$  represents a carbon or silicon atom and R, R' and R'' represent, independently, the hydrogen atom or an alkyl radical;

$L_3$  represents a radical of formula  $-E'_{15}(R'_{15})(R''_{15})$  in which  $E'_{15}$  is a nitrogen or phosphorus atom, and  $R'_{15}$  and  $R''_{15}$  represent, independently, a hydrogen atom or a radical of formula  $-E'_{14}TT'T''$  in which  $E'_{14}$  represents a carbon or silicon atom and T, T' and T'' represent, independently, the hydrogen atom or an alkyl radical.

Preferably, M represents a zinc atom. Preferably also,  $R_M$  represents a methyl radical; A and B represent, independently, a carbon chain with 2 carbon atoms;  $L_1$  and  $L_2$  represent, independently, a radical of formula  $-E_{15}(R_{15})-$  in which  $E_{15}$  is a nitrogen atom and  $R_{15}$  represents a hydrogen atom, a methyl, ethyl, propyl, isopropyl radical or a radical of formula  $-E_{14}RR'R''$  in which  $E_{14}$  represents a silicon atom and R, R' and R'' represent, independently, the hydrogen atom or a methyl, ethyl, propyl or isopropyl radical;  $L_3$  represents a radical of formula  $-E'_{15}(R'_{15})(R''_{15})$  in which  $E'_{15}$  is a nitrogen atom, and  $R'_{15}$  and  $R''_{15}$  represent, independently, a hydrogen atom, a methyl, ethyl, propyl, isopropyl radical or a radical of formula  $-E'_{14}TT'T''$  in which  $E'_{14}$  represents a silicon atom and T, T' and T'' represent, independently, the hydrogen atom or a methyl, ethyl, propyl or isopropyl radical.

More particularly, a subject of the invention is the products described hereafter in the examples, in particular the products corresponding to the following formulae:



A subject of the invention is also a process for the preparation of the products of general formula 1 as defined above, characterized in that a product of formula I

$$(\text{L}_1\text{-A-L}_2\text{-B-L}_3)^-, \text{Y}^+ \quad (\text{I})$$

in which  $L_1$ , A,  $L_2$ , B and  $L_3$  have the meanings indicated above and Y represents the hydrogen atom, a metal or a metallic group, is reacted with a product of formula II

$$5 \qquad \qquad \qquad \text{MR}_M Z \quad (\text{II})$$

in which M and R<sub>M</sub> have the meanings indicated above and Z represents a parting group, in order to obtain a product of formula 1 as defined above.

The reaction of a compound of general formula I with a compound of general formula II in order to obtain a compound of general formula 1, can be carried out under an inert atmosphere such as under a freon or argon atmosphere, in an aprotic solvent, at a temperature comprised between -90 and +50° C. The compounds I thus obtained are purified by standard purification methods.

As aprotic solvent, aromatic hydrocarbons such as benzene, toluene; aliphatic hydrocarbons such as pentane, heptane, hexane, cyclohexane; ethers such as diethylether, dioxane, tetrahydrofuran, ethyltertiobutyl ether can be used.

In the Compounds I, Y represents the hydrogen atom, a metal or a metallic group. The metallic group can be a compound of formula  $R'''M_1$  or  $R'''_3M_2$  in which  $R'''$  represents a halogen atom, or indifferently, an alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy or aryloxy radical as previously defined,  $M_1$  is a zinc or mercury atom or an alkaline-earth such as magnesium and  $M_2$  a tin or lead atom; preferably, the metallic group is chosen from the MgBr, ZnMe, SnMe<sub>3</sub>, SnBu<sub>3</sub> or PbMe<sub>3</sub> groups. The metal can be an alkali metal chosen from lithium, sodium or potassium.

In the compounds II, Z represents a parting group such as a halogen atom, an alkyl, cycloalkyl, alkoxy, aryl, aryloxy, amino, alkylamino or dialkylamino group as previously defined, or also a methanesulphonyloxy, a benzenesulphonyloxy, p-toluenesulphonyloxy group.

The starting products of formula I are known products or can be prepared from known products. For their synthesis, the following references can be mentioned: Cloke et al., J. Chem. Soc., Dalton Trans. (1995) 25; Wilkinson and Stone, Comprehensive Organometallic Chemistry (1982) vol. 1, 557.

The products of formula II are commercially available or can be manufactured by methods known to a person skilled in the art.

A subject of the invention is also the use of the products of formula 1 as defined above, as catalysts for carrying out (co)polymerization, that is to say of polymerization or copolymerization. Whilst carrying out (co)polymerization, the compounds according to the invention also play the role of chain initiator and/or of regulator.

- 5 The compounds of formula 1 are particularly useful for carrying out the polymerization of heterocycles. The heterocycles can contain one or more heteroatoms of groups 15 and/or 16, and have a size ranging from three to eight members. As an example of heterocycles corresponding to the previous formulation, epoxides, thioepoxides, cyclic esters or thioesters such as lactones, lactams and anhydrides can be mentioned.
- 10 The compounds of formula 1 are also particularly useful for carrying out the (co)polymerization of cyclic esters. As an example of cyclic esters, the polymer cyclic esters of lactic and/or glycolic acid can be mentioned. Random or block copolymers can be obtained depending on whether the monomers are introduced together at the start of the reaction, or sequentially during the course of the reaction.
- 15 A subject of the invention is also a process for the preparation of random or block copolymers, or polymers which consists of bringing into contact one or more monomers, a chain initiator and/or a regulator, a polymerization catalyst and optionally a polymerization solvent, said process characterized in that the chain initiator and/or chain regulator and the polymerization catalyst are represented by the same compound which is chosen from the  
20 compounds of formula (1) as defined above.

The (co)polymerization can be carried out either in solution or in supercooling. When the (co)polymerization is carried out in solution, the reaction solvent can be the (or one of the) substrate(s) used in the catalytic reaction. Solvents which do not interfere with the catalytic reaction itself, are also suitable. As an example of such solvents, saturated or  
25 aromatic hydrocarbons, ethers, aliphatic or aromatic halides can be mentioned.

The reactions are carried out at temperatures comprised between ambient temperature and approximately 250° C; the temperature range comprised between 40 and 200° C is most advantageous. The durations of the reactions are comprised between a few minutes and 300 hours, and preferably between 5 minutes and 72 hours.

- 30 This (co)polymerization process is particularly suitable for obtaining (co)polymers of cyclic esters, in particular the polymer cyclic esters of lactic and/or glycolic acid. The products obtained such as the biodegradable glycolic lactic copolymers, are advantageously used as a support in sustained release therapeutic compositions. The process is also particularly well suited to the polymerization of epoxides, in particular propylene oxide.

The polymers obtained are compounds which can be used for the synthesis of organic liquid crystals or also as semi-permeable membranes.

The invention also relates to the polymers or copolymers which can be obtained by carrying out a process as described above.

- 5 The following examples are presented to illustrate the above procedures and should in no way be considered as limiting the scope of the invention.

**Example 1:**  $[\text{Me}_3\text{SiN(H)CH}_2\text{CH}_2\text{N(H)CH}_2\text{CH}_2\text{NSiMe}_3]\text{ZnMe}$  (in dimer form)

- 4.3 g (17.7 mmol) of  $[(\text{Me}_3\text{SiN(H)CH}_2\text{CH}_2)_2\text{NH}]$  and 30 ml of toluene are successively introduced into a Schlenk tube equipped with a magnetic stirrer and purged under argon.
- 10 The reaction mixture is cooled down to -78 C, then 8.8 ml (17.7 mmol) of a 2M solution of  $\text{ZnMe}_2$  in toluene is introduced. The reaction mixture is brought to ambient temperature then left under agitation for 18 hours at ambient temperature. After evaporating the solvent, an orange oil is obtained. The desired compound is isolated in the form of colourless crystals by crystallization at -20 C from pentane (5 ml) (yield 50 %). This
- 15 compound is characterized by multinuclear magnetic resonance spectroscopy and X-ray diffraction (Figure 1 and Table 1 below).

**Example 2:**  $[\text{Me}_3\text{SiN(H)CH}_2\text{CH}_2\text{N(Me)CH}_2\text{CH}_2\text{NSiMe}_3]\text{ZnMe}$  (in dimer form)

- 1.1 g (4.2 mmol) of  $[(\text{Me}_3\text{SiN(H)CH}_2\text{CH}_2)_2\text{NMe}]$  and 20 ml of toluene are successively introduced into a Schlenk tube equipped with a magnetic stirrer and purged under argon.
- 20 The reaction mixture is cooled down to -78 C, then 2.1 ml (4.2 mmol) of a 2M solution of  $\text{ZnMe}_2$  in toluene is introduced. The reaction mixture is brought to ambient temperature then left under agitation for 3 hours at ambient temperature. After evaporating the solvent, an orange oil is obtained. The desired compound is isolated in the form of white crystals by crystallization at -20° C from pentane (5 ml) (yield 50 %). This compound is
- 25 characterized by multinuclear magnetic resonance spectroscopy.

**Example 3:** preparation of a poly(D,L-lactide)

- 0.045 g (0.14 mmol) of  $[\text{Me}_3\text{SiN(H)CH}_2\text{CH}_2\text{-N(H)CH}_2\text{CH}_2\text{NSiMe}_3]\text{ZnMe}$  and 100 ml of toluene are successively introduced into a Schlenk tube equipped with a magnetic stirrer and purged under argon. The reaction mixture is brought to 80°C. 6.24 g (43.2 mmol) of
- 30 D,L-lactide is then added. The reaction mixture is left under agitation at 80 °C for 42 hours. The polymer is characterized by carbon and proton NMR; the conversion of the monomer is 96 %. According to a GPC analysis (Gel Permea Chromatography) using a calibration carried out from polystyrene (PS) standards polystyrene standards of masses

761 to 400000, the sample is comprised of polymers having high masses ( $M_w = 40400$  Dalton).

**Example 4:** preparation of a block (D,L-lactide / glycolide) copolymer

0.15 g (0.43 mmol) of  $[\text{Me}_3\text{SiN}(\text{H})\text{CH}_2\text{CH}_2\text{-N}(\text{Me})\text{CH}_2\text{CH}_2\text{NSiMe}_3]\text{ZnMe}$ , 3.50 g (24 mmol) of D,L-lactide and 80 ml of toluene are successively introduced into a Schlenk tube equipped with a magnetic stirrer and purged under argon. The reaction mixture is left under agitation at 85 °C for 18 hours. Proton NMR Analysis of the allows verification that the conversion of the monomer is greater than 94 %. 2.25 g (19.4 mmol) of glycolide is added over a period of 11 days to the previous solution maintained under agitation at 80° C. Analysis of an aliquot by proton NMR shows that a copolymer is formed. The ratio of the signal integrals corresponding to the polylactide part (5.20 ppm) and polyglycolide part (4.85 ppm) is 4/1. According to a GPC analysis, using a calibration carried out from PS standards of masses of 761 to 400000, this copolymer is a mixture of macromolecules having similar masses ( $M_w/M_n = 1.63$ ;  $M_w = 2960$  Dalton).

**Example 5:** preparation of a random (D,L-lactide / glycolide) copolymer

0.05 g (0.15 mmol) of  $[\text{Me}_3\text{SiN}(\text{H})\text{CH}_2\text{CH}_2\text{-N}(\text{Me})\text{CH}_2\text{CH}_2\text{NSiMe}_3]\text{ZnMe}$ , 6.66 g (45 mmol) of D,L-lactide and 1.53 g (13 mmol) of glycolide are successively introduced into a Schlenk tube equipped with a magnetic stirrer and purged under argon. The reaction mixture is heated to 180° C for 2 hours. The polymer is characterized by proton NMR; the conversion of monomers is total. The ratio of the signal integrals corresponding to the polylactide part (5.20 ppm) and the polyglycolide part (4.85 ppm) is 4/1. According to a GPC analysis, using a calibration carried out from PS standards of masses of 761 to 400000, the sample comprises polymers with a polydispersity ( $M_w/M_n$ ) of 2.27 and molecular weight ( $M_w$ ) of 16271 Dalton.

**Example 6:** preparation of a random (D,L-lactide / glycolide) copolymer having a lactide/ glycolide composition close to 70/30

0.024 g (0.073 mmol) of  $[\text{Me}_3\text{SiN}(\text{H})\text{CH}_2\text{CH}_2\text{-N}(\text{H})\text{CH}_2\text{CH}_2\text{NSiMe}_3]\text{ZnMe}$ , 1.98 g (13.6 mmol) of D,L-lactide and 0.68 g (5.8 mmol) of glycolide are successively introduced into a Schlenk tube equipped with a magnetic stirrer and purged under argon. The reaction mixture is left under agitation at 180° C for 2 hours. Analysis by proton NMR allows verification that the conversion of the monomers is 98 % lactide and 100% glycolide. The ratio of the signal integrals corresponding to the polylactide part (5.20 ppm) and the polyglycolide part (4.85 ppm) the composition of the copolymer to be evaluated at 65% of lactide and 35% of glycolide. According to a GPC analysis, using a calibration carried out



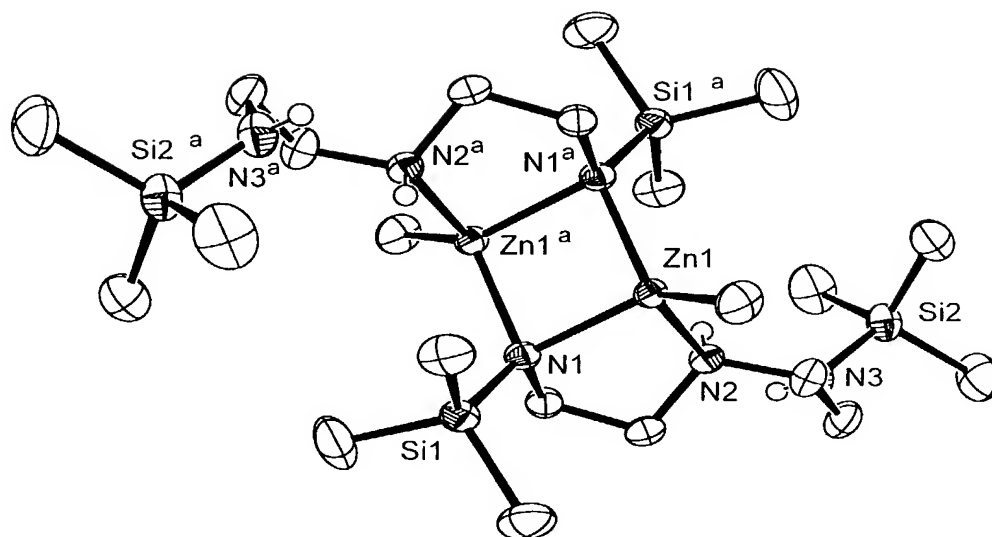
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from PS standards of masses 761 to 400000, this copolymer is a mixture of macromolecules ( $M_w/M_n = 2.84$ ) of high masses ( $M_w = 34500$  Dalton).

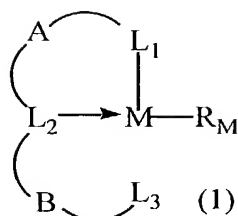
**Table 1:** Lengths of the selected bonds (in Angström) and bond angles (in degrees) for the compound of Example 1

Zn(1)-C(1)	1.989(2) Å	C(5)-C(6)	1.519 (3) Å
Zn(1)-N(1)	2.086(2) Å	C(6)-N(2)	1.475 (3) Å
Zn(1)-N(2)	2.145 (2) Å	N(2)-C(7)	1.472 (3) Å
Zn(1)-N(1A)	2.084 (2) Å	N(2)-C(7)	1.472 (3) Å
N(1)-If(1)	1.725 (2) Å	C(7)-C(8)	1.519 (3) Å
N(3)-If(2)	1.711 (2) Å	C(8)-N(3)	1.453 (3) Å
N(1)-C(5)	1.483 (3) Å		
N(1)-Zn(1)-N(2)	85.1(1) °	Si(1)-N(1)-Zn(1)	119.5 (1) (2) °
N(1)-Zn(1)-C(1)	129.2 (1) °	Si(1)-N(1)-Zn(1A)	120.8 (1) °
N(1)-Zn(1)-N(1A)	93.7 (1) °	Si(1)-N(1)-C(5)	112.7 (1) °
N(2)-Zn(1)-C(1)	112.1 (1) °	Zn(1)-N(1)- Zn(1A)	86.3 (1) °
N(2)-Zn(1)-N(1A)	109.4 (4) °	Zn(1)-N(1)-C(5)	106.2 (1) °
C(1)-Zn(1)-N(1A)	120.1 (1) °	Zn(1A)-N(1)-C(5)	108.0 (1) °

Fig. 1



1. Compounds of general formula 1



5 in which  
M represents an element of group 12;  
R<sub>M</sub> represents the hydrogen atom, a halogen atom, or an alkyl, cycloalkyl, aryl,  
alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio, arylthio, amino,  
alkylamino, dialkylamino, cycloalkylamino, di(cycloalkyl)amino,  
10 alkyl(cycloalkyl)amino, arylamino, diarylamino, alkylaryl amino or  
(cycloalkyl)aryl amino radical;  
A and B represent, independently, a carbon chain of 2 to 4 carbon atoms, optionally  
substituted by one or more of the following substituted or non-substituted  
alkyl, cycloalkyl or aryl radicals, in which said substituent is a halogen  
15 atom, an alkyl, nitro or cyano radical;  
L<sub>1</sub> and L<sub>2</sub> represent, independently, a group of formula -E<sub>15</sub>(R<sub>15</sub>)- in which  
E<sub>15</sub> is an element of group 15 and  
R<sub>15</sub> represents the hydrogen atom; one of the following substituted or  
non-substituted alkyl, cycloalkyl or aryl radicals, in which said substituent is  
20 a halogen atom, an alkyl, nitro or cyano radical; a radical of formula  
-E<sub>14</sub>RR'R" in which E<sub>14</sub> is an element of group 14 and R, R' and R" represent,  
independently, the hydrogen atom or one of the following substituted (by  
one or more identical or different substituents) or non-substituted alkyl,  
cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio or  
25 arylthio radicals, in which said substituent is a halogen atom, the alkyl, nitro  
or cyano radical; or a radical of formula -SO<sub>2</sub>Q in which Q represents a  
halogen atom, an alkyl, haloalkyl or aryl radical optionally substituted by

L<sub>3</sub> indifferently represents a group of formula -E'<sub>15</sub>(R'<sub>15</sub>)(R''<sub>15</sub>) or -E<sub>16</sub>(R<sub>16</sub>) in which

$E_{16}$  is an element of group 16 and

20     2. Compounds of formula 1 as defined in claim 1, characterised in that they are presented in the form of a monomer or a dimer.

R<sub>M</sub> represents an alkyl group;

L<sub>1</sub> and L<sub>2</sub> represent, independently, a radical of formula -E<sub>15</sub>(R<sub>15</sub>- in which E<sub>15</sub> is a nitrogen or phosphorus atom and R<sub>15</sub> represents a hydrogen atom or a radical of formula -E<sub>14</sub>RR'R" in which E<sub>14</sub> represents a carbon or silicon atom and R, R' and R" represent, independently, the hydrogen atom or an alkyl radical;

30 L<sub>3</sub> represents a radical of formula -E'<sub>15</sub>(R'<sub>15</sub>)(R''<sub>15</sub>) in which E'<sub>15</sub> is a nitrogen or phosphorus atom, and R'<sub>15</sub> and R''<sub>15</sub> represent, independently, a hydrogen atom or a radical of formula -E'<sub>14</sub>TT'T'' in which E'<sub>14</sub> represents a carbon or silicon atom and T, T' and T'' represent, independently, the hydrogen atom or an alkyl radical.

4. Compounds of general formula 1 as defined in one of claims 1 to 3, characterized in  
35 that M represents a zinc atom.

5. Compounds of general formula 1 as defined in one of claims 1 to 4, characterized in that
- $R_M$  represents a methyl radical;
- A and B represent, independently, a carbon chain of 2 carbon atoms;
- 5  $L_1$  and  $L_2$  represent, independently, a radical of formula  $-E_{15}(R_{15})-$  in which  $E_{15}$  is a nitrogen atom and  $R_{15}$  represents a hydrogen atom, a methyl, ethyl, propyl, isopropyl radical or a radical of formula  $-E_{14}RR'R''$  in which  $E_{14}$  represents a silicon atom and R, R' and R'' represent, independently, the hydrogen atom or a methyl, ethyl, propyl or isopropyl radical;
- 10  $L_3$  represents a radical of formula  $-E'_{15}(R'_{15})(R''_{15})$  in which  $E'_{15}$  is a nitrogen atom, and  $R'_{15}$  and  $R''_{15}$  represent, independently, a hydrogen atom, a methyl, ethyl, propyl, isopropyl radical or a radical of formula  $-E'_{14}TT'T''$  in which  $E'_{14}$  represents a silicon atom and T, T' and T'' represent, independently, the hydrogen atom or a methyl, ethyl, propyl or isopropyl radical.
6. Compounds of general formula 1 as defined in one of claims 1 to 4 and corresponding
- 15 to the following formulae:
- $[Me_3SiN(H)CH_2CH_2N(Me)CH_2CH_2NSiMe_3]ZnMe$ ;
- $[Me_3SiN(H)CH_2CH_2N(H)CH_2CH_2NSiMe_3]ZnMe$ .
7. Compounds of formula 1 as defined in claim 6, characterised in that they are presented in dimer form.
- 20 8. Process for the preparation of the products of general formula 1 as defined in claim 1, characterized in that a product of formula I
- $$(L_1-A-L_2-B-L_3)^-, Y^+ \quad (I)$$
- in which  $L_1$ , A,  $L_2$ , B and  $L_3$  have the meanings indicated in claim 1 and Y represents the hydrogen atom, a metal or a metallic group, is reacted with a product of formula II
- 25  $MR_MZ \quad (II)$
- in which M and  $R_M$  have the meanings indicated in claim 1 and Z represents a parting group, in order to obtain a product of formula 1.
9. Use of the products of formula 1 as defined in any one of claims 1 to 7, as polymerization or copolymerization catalyst.
- 30 10. Use according to claim 9 for the polymerization or copolymerization of heterocycles, in particular epoxides such as propylene oxide.
11. Use according to claim 9, for the polymerization or copolymerization of cyclic esters, in particular the polymer cyclic esters of lactic and/or glycolic acid.

10 **13.** Process according to claim 12, characterized in that the monomer is chosen from the epoxides, and in particular propylene oxide, or the cyclic esters, and in particular the polymer cyclic esters of lactic and/or glycolic acid.

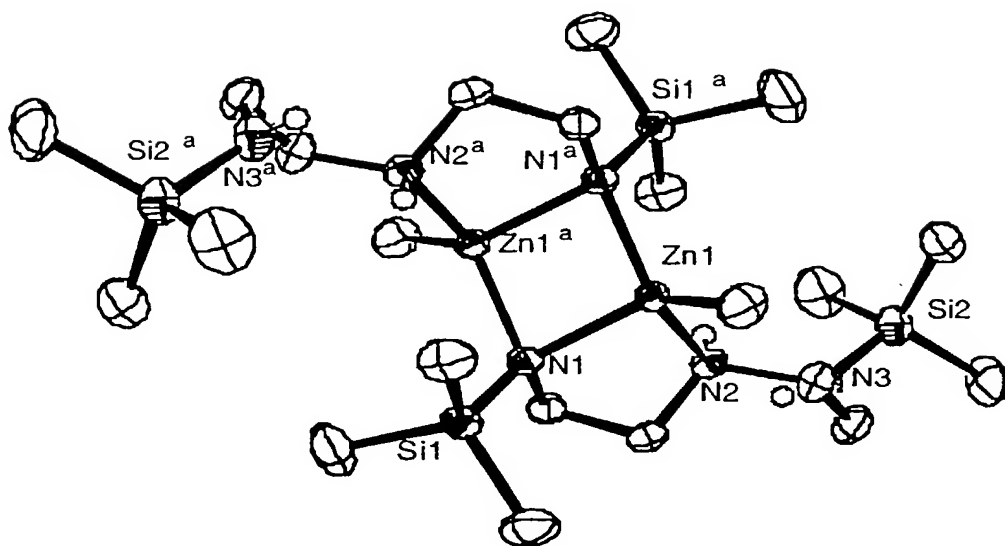
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**ABSTRACT**

The present invention relates to new compounds having an element of group 12 and having a tridentate ligand, a process for their preparation and their use in particular as a polymerization catalyst.



Fig. 1



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**DECLARATION FOR  
UTILITY OR DESIGN  
PATENT APPLICATION**☒ Declaration OR  
Submitted  
with Initial Filing ☐ Declaration  
Submitted after  
Initial Filing

Attorney Docket Number

First Named Inventor

H. NGUYEN N. GOC

**COMPLETE IF KNOWN**

Application Number

Filing Date

Group Art Unit

Examiner Name

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

POLYMERISATION CATALYSTS

(Title of the invention)

the specification of which

☐ is attached hereto  
OR☒ was filed on (MM/DD/YYYY)

06/23/2000

as United States Application Number or PCT International

Application Number

PCT/FR00/01753

and was amended on (MM/DD/YYYY)

(if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code §119 (a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365 (a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached?	
				YES	NO
99 401585.7	Europe	06/25/1999	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>

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I hereby claim the benefit under Title 35, United States Code § 120 of any United States application(s), or § 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)

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As a named inventor, I hereby appoint the following registered practitioner(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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Jordan B. Bierman	18,629		
Donald C. Lucas	31,275		
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

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Inventor's Signature						Date	November 22 <sup>nd</sup> , 2001

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☒ Additional inventors are being named on supplemental sheet(s) attached hereto



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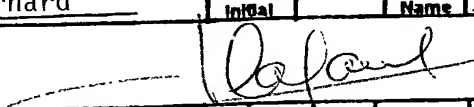
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## DECLARATION

## ADDITIONAL INVENTOR(S) Supplemental Sheet

<b>Name of Additional Joint Inventor, if any:</b>				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
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<b>Name of Additional Joint Inventor, if any:</b>				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
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Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
Post Office Address							
Post Office Address							
City		State		Zip		Country	
<b>Name of Additional Joint Inventor, if any:</b>				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
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Inventor's Signature					Date		
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Post Office Address							
City		State		Zip		Country	
<b>Name of Additional Joint Inventor, if any:</b>				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name		Middle Initial		Family Name		Suffix	e.g. Jr.
Inventor's Signature					Date		
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<b>DECLARATION</b>	<b>REGISTERED PRACTITIONER INFORMATION (Supplemental Sheet)</b>
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Name	Registration Number	Name	Registration Number